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ON A NEW DISTRIBUTION FORMULA FOR MOLECULES OF REAL GASES AND FOR IONS OF STRONG ELECTROLYTES IN SOLUTION

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ABSTRACT. A distribution formula for molecules of finite size in fields of forces, and of ions of strong electrolytes in solution, which was found to be very useful for development of a new theory of real gases and of strong electrolytes in solutions, was deduced by Dutta (1947, 1948, 1951a, 1951b, 1952, 1959) and by Dutta and Bagchi (1950). In these deductions, the phase-space is split into momental and configurational spaces, the configurational space is divided into layers of different potential energies which are again divided into small cells, and then distributions of image points in momental and configurational spaces are considered separately. Here, over and above all these, the notion of coarse-graining has been introduced for determining distributions in the configurational space. A new distribution-formula, which may be useful in the theory of real gases and of strong electrolytes in solution, is obtained.

INTRODUCTION

For statistical considerations of an assembly of a large number of particles, the phase-space is conveniently divided into cells of suitably small volume and then the distributions of particles (really, then image-points) in these cells are considered by treating the states of a particle by points in a cell as equivalent (cf., Ehrenfest P. and T., 1959). This procedure is practically the same as the grouping of observational data in statistical analysis. Its significance and justification from information-theoretical and statistical stand-point can be seen in the book of Kullback (1959) and in some recent discussions (Dutta, 1965, 1966a and 1966b).

Before the formulation of Heisenberg's uncertainty principle, the measure of the volume of the small cells was arbitrary. But simple arguments based on this principle (cf. Dutta, 1965, 1966a and 1966b) lead to the value, h^3, for the volume of the elementary cells, h being the Planck constant.

In a number of papers (Dutta, 1947, 1948, 1951a, 1951b, 1952, 1959, 1965, 1966a; Dutta and Bagchi, 1950; Dejak, 1959), for the consideration of the volume of exclusion of particles (molecules, ion, etc) supposed to be rigid, i.e., for the consideration of the short-ranged repulsive interactions between particles of the type,

$$F(r_{ij}) = \begin{cases} 0 & \text{for } r_{ij} > r_0 \\ \infty & \text{for } r_{ij} \leqslant r_0 \end{cases}$$

r_{ij} being the distance between the i-th and the j-th particle, and r_0 being a characteristic constant for pair of particles of a particular kind, generally taken as the

sum of the radius of the particles in the pair, the configurational space is divided in small cells of volume, b, equal to the volume of exclusion of a particle and the particles are assumed to be distributed in such a manner that each cell may either remain vacant or be occupied by a single particle. If there be other forces of some regular types the configurational space is also divided into potential layers, which are again supposed to contain a large number of the above cells, and then, the distributions of particles are to be considered in these cells (Dutta, 1951a, 1951b; Dutta and Bagchi, 1950, Dejak, 1959). By forces of some regular type, it is meant that the gradient of forces is large compared to the dimension of particles and small compared to the volume of the container. Now, when the assembly contains particles of different kinds, the method has been modified suitably by introducing different volumes, b_1, b_2, b_{12} for pair of different kinds and then by calculating the theomodynamic probability suitably (Dutta 1951b, Dutta and Bagchi, 1950, Dejak, 1959).

Now, in calculations of activity coefficients for strong electrolytes in solution, it is seen that better results are obtained if different values of b_+ and b_- are chosen suitably in different ranges of concentrations. So, it has appeared that it may be possible to deduce more useful results, if b is interpreted suitably and slightly differently. Here, it is done simply after the introduction of coarse-grained distribution, as already mentioned earlier (Dutta, 1965).

We shall take b, the volume of the cell, as a bit arbitrary parameter which is greater than b_0, the volume of exclusion and is to be chosen suitably to the fit the experimental value. b is taken to be such a small volume that it is quite sufficient to specify the position of a particle by stating that it is in a particular cell. The equation of an ideal gas can be deduced simply by specifying the position of a particle to be anywhere in the total volume V of the container, i.e., $b = V$ (cf. Falkenhagen, 1950). In denser systems and in the presence of an external external field and or of a field of interactions, more accurate specification is necessary, i.e., $b_0 \leqslant b < V$. Now, if $r = [b/b_0]$ the integer just less than b/b_0, it is easy to see that a cell may be vacant or occupied by utmost r number of particles. In this respect, it is similar to Gentile statistics. For simplicity, we first consider the case where the forces other than the short-ranged repulsive force for rigid particles are absent. After that, we consider the case where there are other forces of regular type over and above the above short-ranged force. At the end, mixtures of particles of two different types is discussed. Except the introduction of the notion of corse-grained distribution other notions are similar to those develope earlier by the author.

ASSEMBLY OF PARTICLES OF FINITE SIZE

The thermodynamic probability is

$$W = \frac{[V/b]!}{\prod_l n_l! \,[V/b - N]!} \cdot \frac{N!}{\prod_l a_m!} \tag{2.01}$$

where V is the volume of the container, N the number of particles, N_l the number of cells occupied by b particles, and a_m the number of particles with kinetic energy, $\epsilon_l \cdot [V/v]$ is the integer just less than (V/b). As in gases (V/b) is generally very large, so in future discussion we shall neglect their difference and always write (V/b). After using Stirling's formula and taking logarithm, we have

$$\log W = \left(\frac{V}{b}\right) \log \left(\frac{V}{b}\right) - \sum_l N_l \log N_l + N_l \log N - \sum_l a_m \log a_m \quad \ldots \quad (2.02)$$

This is to be maximised subject to the condition that

$$\sum_{l=0}^{r} N_l = \left(\frac{V}{b}\right) \quad \ldots \quad (2.03)$$

$$\sum_{l=1}^{r} lN_l = N \quad (2.04)$$

$$\Sigma a_m = N \quad (2.05)$$

$$\Sigma a_m \epsilon_m = E \quad (2.06)$$

E being the total energy.

Then, by usual variations, we get

$$N_l = e^{-\nu - \nu_1 l} \quad \ldots \quad (2.07)$$

and

$$a_m = e^{\lambda - \epsilon_m} \quad \ldots \quad (2.08)$$

Therefore,

$$S = k \log W_{max} = k\left[\left(\frac{V}{b}\right) \log \left(\frac{V}{b}\right) + \nu\left(\frac{V}{b}\right) + \nu_1 N + \lambda N + \mu E\right] \quad \ldots \quad (2.09)$$

From well-known thermodynamic relation we have

$$\mu = \frac{1}{k}\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{kT} \quad \ldots \quad (2.10)$$

T being the temperature.

Then, from (2.05) we have

$$e^{\lambda} = \frac{1}{N} \sum_m e^{-\epsilon_m/kT} = \frac{1}{N} \int\int\int e^{-\frac{p_x^2 + p_y^2 + p_z^2}{kT}} \frac{dp_x dp_y dp_z}{h^3/b}$$

$$= \frac{b}{Nh^3} (2\pi mkT)^{3/2} \quad \ldots \quad (2.11)$$

From (2.03), we have

$$e^{\nu} = \frac{b}{V} \sum_{l} e^{-\nu_1 b} = \frac{b}{V} \frac{1-e^{-(r+1)\nu_1}}{1-e^{\nu_1}} \qquad \ldots \quad (2.12)$$

From (2.04), we have,

$$e^{\nu} = \frac{1}{N} \sum_{l=1}^{r} l e^{-\nu_1 l}$$

or

$$\frac{Nb}{V} = \frac{\Sigma l e^{-\nu_1 l}}{\Sigma e^{-\nu_1 l}} = \frac{\partial}{\partial \nu_1} \left\{ \log \left(\sum_{l} e^{-\nu_1 l} \right) \right\}$$

$$= \frac{1}{e^{\nu_1}-1} - \frac{(r+1)}{e^{(r+1)\nu_1}-1} \qquad \ldots \quad (2.13)$$

Thus, all the parameters (Lagrange's undetermined multipliers), entering in the calculation can be determined. As the case when $r = 1$, has already been completely worked out (Dutta, 1957) in actual applications, r will be two or three and so calculations appear to be not difficult. From (2.09), S is known in terms of V, T on substitution of values of ν, ν_1, λ, μ and by well-known thermodynamic relations, expressions of other thermodynamic functions can be easily calculated.

ASSEMBLY OF PARTICLES OF FINITE SIZE IN PRESENCE OF OTHER FIELDS OF FORCES

As in earlier papers, (Dutta, 1951a, 1952b, 1959), it is assumed that the forces, other than the short-ranged force associated with rigidity, are such that the entire configurational space is divided into potential energy layers of potential energies $\psi_1, \psi_2, \ldots$ of corresponding volumes, $V_1, V_2, \ldots$ which are small compared to the total volume V but large compared b. As before the thermodynamic probability can be written as

$$W = \prod_{n} \frac{(V_n/b)_l}{\prod_{l} N_{nl}!} \cdot \frac{N!}{\pi_m a_m!} \qquad \ldots \quad (3.01)$$

where N_{nl} is the number of cells in the n-th layer which are occupied by l particles and other symbols have interpretations, same as in the preceeding article.

As usual, after using Stirling formula for factorial, and then taking logarithm, we get,

$$\log W = \left[\sum_{n} \left\{ \left(\frac{V_n}{b} \right) \log \left(\frac{V_n}{b} \right) - \sum_{l=0}^{r} N_{nl} \log N_{nl} \right\} + N \log N - \sum_{m} a_m \log a_m \right] \qquad \ldots \quad (3.02)$$

This is to be maximised, subject to the condition that

$$\sum_{nl} N_{nl} = \sum_n \left(\frac{V_n}{b} \right) = \left(\frac{V}{b} \right) \quad \ldots \quad (3.03)$$

$$\sum_l l N_{nl} = \sum_n N_n = N \quad \ldots \quad (3.04)$$

$$\sum_m a_m = N \quad \ldots \quad (3.05)$$

and

$$\sum_m a_m \epsilon_{in} + \sum_n (\sum_l l N_{nl}) \psi_n = E \quad \ldots \quad (3.06)$$

After usual variations, we get

$$\sum_{n,l} N_{nl} (\log N_{nl} + \nu + \nu_1 l + \mu l \psi_n) + \sum_l \Delta a_l (\log a_l + \lambda + \mu \epsilon_l) = 0$$

Then,

$$N_n = e^{-\nu - \nu_1 l - \mu l \psi_n} \quad \ldots \quad (3.07)$$

$$a_m = e^{-\lambda - \mu \epsilon_m} \quad \ldots \quad (3.08)$$

$$S = k \log W_{max} = k \left[\sum_n \left(\frac{V_n}{b} \right) \log \left(\frac{V_n}{b} \right) + \nu \left(\frac{V}{b} \right) + \right.$$

$$\left. + \nu_1 N + \lambda N + \mu E \right] \quad \ldots \quad (3.09)$$

In the usual way the temperature can be introduced by the thermodynamic relation as

$$\mu = \frac{1}{k} \left(\frac{\partial S}{\partial E} \right)_{V, N} = \frac{1}{kT} \quad \ldots \quad (3.10)$$

Then,

$$e^{\lambda} = \frac{1}{N} \sum_m e^{-\epsilon_s / kT} = \frac{1}{N} \frac{b}{h^3} (2\pi m k T)^{3/2} \quad \ldots \quad (3\ 11)$$

From (3.03), we have

From (3.03), we have

$$e^{\nu} = \left(\frac{b}{V} \right) \sum_n \frac{1 - e^{-(r+1)\left(\nu_1 + \frac{\psi_n}{kT} \right)}}{1 - e^{-(\nu_1 + \psi_n / kT)}} \quad \ldots \quad (3.12)$$

and

$$N_n = \frac{V_n}{b} \left[\frac{1}{e^{(\nu_1 + \psi_n / kT)} - 1} - \frac{(r+1)}{e^{(r+1)(\nu_1 + \psi_n / kT)} - 1} \right. \quad \ldots \quad (3.13)$$

The equation (3.12) gives an expression of ν in terms of ν_1 The equation (3.13) is the new distribution ofrmula. The parameter, ν_1, is determined (at least theoretically) from the restriction (3.04).

ASSEMBLY OF PARTICLES OF TWO DIFFERENT TYPES

Now we consider an assembly consisting of N_1 and N_2 particles of the first and the second types of masses, m_1 and m_2 respectively. We suppose that the forces are of regular type, so that the configurational space can be divided into potential layers of potential $-\phi_1$, $-\phi_2$, ... $-\phi_n$... so that the potential energies in the n-th layer of particles of the first and the second type are $m_1\phi_n$ and $m_2\phi_n$ respectively. These layers are again divided into cells of volume b. If b_1 and b_2 denote the exclusion volume of the first and the second types for particles of the same types and $b_{12}(=b_{21})$ denote the same for particles of different types and if we write

$$r_1=\left[\frac{b}{b_1}\right],\ r_2=\left[\frac{b}{b_2}\right],r_{1j}=\left[\frac{b-jb_{12}}{b_1}\right],\ r_{l2}=\left[\frac{b-lb_{12}}{b_2}\right] \qquad \ldots\ (4.01)$$

then a cell may remain vacant or may be occupied utmost by r_1 particles only of the first type, or utmost by r_2 particles only of the second type, or utmost by r_1 particles of the first type when it is already occupied by j particles of the second type or utmostly r particles of the second type when it is already occupied by l particles of the first type.

We write the thermodynamics probability as follows :

$$W=\prod_n \frac{(V_n/b)!}{\pi N_{nij}!}\cdot\frac{N_1!}{\pi_l a_{1l}!}\cdot\frac{N_2!}{\pi_n a_{2m}!} \qquad \ldots\ (4.02)$$

where N_{nij} = the number of cells, in the n th layers, occupied by i particles of the first type and j particles of the second type,

a_{1m} = the number of particles of the first type with the kinetic-energy, ϵ_{1m},

and a_{2m} = that of the second type with the kinetic energy, ϵ_{2m}.

After using Stirling's approximate formula for factorials and then taking logarithm, we have

$$\log W=\sum_n\left\{\left(\frac{V_n}{b}\right)\log\left(\frac{V_n}{b}\right)-\sum_{ij}N_{nij}\log N_{nij}\right\}$$

$$+N_1\log N_1+N_2\log N_2-\sum_l a_{1l}\log a_{1m}-\sum_m a_{2m}\log aa_{2m} \qquad \ldots\ (4.03)$$

This is to be maximised subject to the following conditions :

$$\sum_{nlj} N_{nlj} = \sum \frac{V_n}{b} = \frac{V}{b} \qquad \ldots (4.04)$$

$$\sum_{nlj} lN_{nlj} = \sum_{n} N_{1n} = N_1 \qquad \ldots (4.05)$$

$$\sum_{nlj} jN_{nlj} = \sum_{n} N_{2n} = N_2 \qquad \ldots (4.06)$$

$$\sum_{l} a_{1m} = N_1 \qquad \ldots (4.07)$$

$$\sum_{} a_{2m} = N_2 \qquad \ldots (4.08)$$

$$\sum_{l} a_{1m}\epsilon_{1m} + \sum_{m} a_{2m}\epsilon_{2m} + \sum_{nlj} N_{nmj}(im_1 + jm_2)\phi_n = E \qquad (4.09)$$

where the volume, V, of the container, total numbers, N_1 and N_2, of particles and the total energy E, are to be taken as constant.

After usual variation, we get

$$N_{nlj} = e^{-\nu - \nu_1 l - \nu_2 j - \mu(m_1 l + m_2 j)\varphi_n} \qquad \ldots (4.10)$$

$$a_{1m} = e^{-\lambda_1 - \mu\epsilon_{1m}} \qquad \ldots (4.11)$$

$$a_{2m} = e^{-\lambda_2 - \mu\epsilon_{2m}} \qquad \ldots (4.12)$$

where ν, ν_1, ν_2, λ_1, λ_2, μ are Lagrange's undetermined multipliers to be interpreted suitably. Then by Boltzmann hypothesis after using the relations (4.10, 4.12), we get

$$S = k \log W_{max} = k\Big[\sum_{n} \Big(\frac{V_n}{b} \Big) \log \Big(\frac{V_n}{b} \Big) + \nu \Big(\frac{V}{b} \Big) + N_1 \log N_1 + N_2 \log N_2 + (\lambda_1 + \nu_1)N_1 + (\lambda_2 + \nu_2)N_2 + \mu E \qquad \ldots (4.13)$$

As usual, by the well-known thermodynamic relation, we have

$$\mu = \frac{1}{k} \Big(\frac{\partial S}{\partial E} \Big)_{V, N_1, N_2} = \frac{1}{kT} \qquad \ldots (4.14)$$

By the equation (4.07) and (4.08), we have

$$e^{\lambda_1} = \frac{1}{N_1} \cdot \frac{b}{h^3} (2\pi m_1 kT)^{3/2} \qquad \ldots (4.15)$$

$$e^{\lambda_2} = \frac{1}{N_2} \cdot \frac{b}{h^3} (2\pi m_2 kT)^{3/2} \quad \ldots \quad (4.16)$$

By the equation (4.04), we have

$$e^{\nu} = \left(\frac{b}{V}\right) \sum_{nlj} e^{-\nu_1 l - \nu_2 j - (2m_1 + jm_2)\frac{\phi_n}{RT}} \quad \ldots \quad (4.17)$$

This equation gives ν as a function of ν_1, ν_2, m_1, m_2 etc. Then, by (4.15) and (4.06) ν_1 and ν_2 are to be determined.

Now, also we have

$$\frac{V_n}{b} = e^{-\nu} \sum_{lj} e^{-\nu_1 l - \nu_2 j - (lm_1 + jm_2)\frac{\phi_n}{kT}} \quad \ldots \quad (4.18)$$

$$N_{1n} = e^{-\nu} \sum_{lj} ie^{-\nu_1 l - \nu_2 j - (lm_1 + jm_2)\frac{\phi_n}{RT}} \quad \ldots \quad (4.19)$$

and

$$N_{2n} = e^{-\nu} \sum_{lj} je^{-\nu_1 l - \nu_2 j - (lm_1 + jm_2)\frac{\phi_n}{RT}} \quad \ldots \quad (4.20)$$

Then, after simple calculations, we get

$$N_{1n} = \frac{V_n}{b} \cdot \frac{\partial}{\partial \nu_1} \log \left\{ \sum_{lj} e^{-\nu_1 l - \nu_2 j - (lm_1 + jm_2)\frac{\phi_n}{RT}} \right\} \quad \ldots \quad (4.21)$$

$$N_{2n} = \frac{V_n}{b} \cdot \frac{\partial}{\partial \nu_2} \log \left\{ \sum e^{-\nu_1 l - \nu_2 j - (lm_1 + jm_2)\frac{\phi_n}{RT}} \right\} \quad \ldots \quad (4.22)$$

These are the distribution formulae in a binary mixture in most general form. The evaluation of the series within the logarithms, in a closed form, appears to be very complicated. Moreover, it is also very difficult to express the summation within the logarithms as a symmetric function of the characteristic quantities associated with particles of different quantities, since the summation of j first and the over i is apparently different from that of i first and then over j. But, the nature of the problems suggests that the expression within logarithms should be symmetric with respect to the characteristic quantities, associated with particles of different types. We postpone the general discussion at present. Here, we consider in details the case which is comparatively much simple to evaluate and also useful for applications.

Case when $b_{12} = 0$, i.e. b_{12} is negligible compared to b_1 and b_2 :

Here, $r_{1j} = r_1$, and $r_{b2} = r_2$,

for all i and j

Now,

$$\sum_{ij} e^{-\nu\left(1+\frac{m_1\phi_n}{RT}\right)i-\left(\nu_2+\frac{m_2\phi_n}{RT}\right)j}$$

$$= \left\{\frac{1-e^{-\left(\nu_1+\frac{m_1\phi_n}{RT}\right)(r_1+1)}}{1-e^{-\left(\nu_1+\frac{m_1\phi_n}{RT}\right)}}\right\}\left\{\frac{1-e^{-\left(\nu_2+\frac{m_2\phi_n}{RT}\right)(r_2+1)}}{1-e^{\left(\nu_2+\frac{m_2\phi_n}{RT}\right)}}\right\}$$

Then,

$$N_{1n} = \frac{V_n}{b}\left\{\frac{1}{e^{-\nu_1+\frac{m_1\varphi_n}{RT}}-1} - \frac{(r_1+1)}{e^{(r_1+1)\left(\nu_1+\frac{m_1\varphi_n}{RT}\right)}-1}\right\} \quad \ldots \quad (4.23)$$

$$N_{2n} = \frac{V_n}{b}\left\{\frac{1}{e^{\nu_2+\frac{m_2\varphi_n}{TR}}-1} - \frac{(r_2+1)}{e^{(r_2+1)\left(\frac{m_2\varphi_n}{RT}\right)}-1}\right\} \quad \ldots \quad (4.24)$$

These are the now distribution formulae in this case for binary mixtre. Of course, the discussion can be extended for a mixture of more than two components and the distribution will be similar to those given by (4.23) and (4.24).

ASEMBLY OF IONS OF STRONG ELECTROLYTES IN SOLUTION

In case of ions of strong electrolytes in solution the average minimum approach of ions of opposite charges is always expected to be bery small compared to that of ions of opposite charge i.e. $b_{+-} << b_+$ and b_-. In actual calculations, (Eigen and Wicke, 1951, Dutta, 1952, 1953; Dutta and Sengupta, 1954) b_{+-} is taken to be zero. So calculations quite similar to the preceeding articles leae to the distribution formulae for ions given by the following expressions :

$$N_{+n} = \frac{V_n}{b}\left\{\frac{1}{e^{\nu_+ + \frac{e_+\phi_n}{RT}}-1} - \frac{(r_+ +1)}{e^{(r_+ +1)\left(\nu_+ + \frac{e_+\varphi_n}{RT}-1\right)}}\right\} \quad \ldots \quad (5.01)$$

$$N_{-n} = \frac{V_n}{b}\left\{\frac{1}{e^{\nu_- + \frac{e_-\varphi_n}{RT}}-1} - \frac{(r_- +1)}{e^{(r_- +1)\left(\nu_- + \frac{e_-\varphi_n}{RT}-1\right)}}\right\} \quad \ldots \quad (5.02)$$

where N_{+n} and N_{-n} are respectively number of ions of positive and negative charges in the n-th layer of electric potential, $-\phi_n$, e_+ and e_- are charges of positive ions and negative ions, and w_+, w_-, r_+, r_- have interpretations similar to those of the preceeding article.

CONCLUDING REMARKS

It can be easily seen that all calculations reduce to those made earlier (Dutta, 1947, 1948, etc.), if the volume, b, of the cell is taken to be equal to thee xclusion volume of the particles. From this stand-point the formulae proposed here are generalisation of those proposed earlier.

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REFERENCES

Dejak, C. 1959, *Proceeding of International Symposium in Electrolytes*, Pergaman Press
Dutta, M. 1947, *Proc. Nat. Inst. Sc. (India)*, **13**, 347.
——— 1948, *Proc. Nat. Inst. Sc. (India)*, **13**, 103
——— 1951, *Proc. Nat. Inst. Sc. (India)*, **16**, 27, 445.
——— 1952, *Proc. Nat. Inst. Sc. (India)*, **17**, 81.
——— 1952, *Naturwiss*, **39**, 108.
——— 1953, *Naturwiss* **40**, 51.
——— 1959, *Proc. Summer Inst. of Theor. Physics at Mussorie (India)*, p 297.
——— 1965, *Science and Culture*, **31**, 231.
——— 1966a, *New Statistical Theories of Real Gases and Electrolytes in Solution*, Scientific Book Agency, Calcutta, India.
——— 1966b, *Statistical Physics (Foundation)*, World Press, Calcutta, India.
Dutta, M. and Bagchi, S. N. 1950: *Indian J. Phys.*, **24**, 61.
Dutta, M. and Sengupta, M. 1954, *Proc. Nat. Inst. Sc. (India)*, **20**, 1.
Ehrenfest, P. and Ehrenfest T. 1959, *The conceptual Fundations of the Statistic Approach in Mechanics*, Connell Univ. Press, N.Y.
Eigen, M. and Wicke, E. 1951, *Naturwiss*, **38**, 453
Falkenhagen, H. 1950, *Statistik und Quantum Theorie*, S Hirzel Verlag, Stugall.
Kullback, S. 1959, *Information Theory and Statistics*, J. Wiley & Sons, N. Y.